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## EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification :  
**09.06.93 Bulletin 93/23**

⑤① Int. Cl.<sup>5</sup> : **C25D 13/22, C09D 5/44**

②① Application number : **90118425.9**

②② Date of filing : **26.09.90**

⑤④ Coating method.

③① Priority : **02.10.89 US 415808**

④③ Date of publication of application :  
**10.04.91 Bulletin 91/15**

④⑤ Publication of the grant of the patent :  
**09.06.93 Bulletin 93/23**

⑧④ Designated Contracting States :  
**DE ES FR GB SE**

⑤⑥ References cited :  
**GB-A- 1 034 517**  
**US-A- 4 421 620**

⑦③ Proprietor : **ILLINOIS TOOL WORKS INC.**  
**3650 West Lake Avenue**  
**Glenview Illinois 60025-5811 (US)**

⑦② Inventor : **Offenburger, Mark J.**  
**2022 Oxford Court**  
**Schaumburg, Illinois 60194 (US)**

⑦④ Representative : **Dipl.-Ing. H. Hauck, Dipl.-Ing.**  
**E. Graalfs, Dipl.-Ing. W. Wehnert, Dr.-Ing. W.**  
**Döring**  
**Neuer Wall 41**  
**W-2000 Hamburg 36 (DE)**

**EP 0 421 247 B1**

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**Description****Background of the Invention**5    **1. Field of the Invention:**

This invention relates generally to coating a conductive substrate by electrodeposition to achieve enhanced corrosion protection and improve cosmetic appeal. More particularly, this invention relates to coating metallic fasteners in bulk quantities using electrodeposition epoxy films.

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**2. Brief Description of the Prior Art:**

It is well known in the art that a conductive substrate can be coated with a composition by electrodeposition. Coating a substrate can serve to protect it against corrosion and/or embellish its ornamental appearance.

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Generally, there are two known types of electrodeposition processes -- anodic electrodeposition and cathodic electrodeposition. Both methods are performed by inducing an electrical current within a coating cell containing a coating compound.

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Anodic electrodeposition is accomplished by first immersing the part to be coated into an electrolytic solution containing the coating composition. A positive charge is imparted onto the conductive substrate to be coated. The negatively charged ionic species of the coating composition then move through the electrolyte medium via the electrophoretic phenomenon to coat the substrate. The coating process continues until the coating composition insulates the substrate at which point the coating process stops. Cathodic electrodeposition brings about similar results by reversing the electrical polarity so that the substrate to be coated acts as a cathode and attracts positively charged ions of the coating composition.

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There are advantages and disadvantages associated with both methods of electrodeposition, but on balance, cathodic electrodeposition is generally preferred by the industry for most applications. Anodic electrodeposition can provide an efficient and uniform coating on both exposed and non-exposed or hidden surfaces of the substrate and the resultant coatings are far superior as compared to those attained by spray and dip coating methods. Over time, however, chemical side effects of the anodic process can destroy the surface of the conductive substrate and cause components thereof to infiltrate the coating material. Such infiltration can reduce corrosion resistance and promote coating discoloration, usually in the form of yellowing. Cathodic electrodeposition generally does not produce as many problems as are associated with anodic electrodeposition. Accordingly, it allows for broader use applications including the use of lighter-colored coatings. Cathodic electrodeposition also provides better gloss and color retention characteristics, as well as superior coating thickness capabilities. Nevertheless, anodic electrodeposition remains the preferred method for certain applications. For example, anodic electrodeposition of an epoxy film provides an ideal primer surface for a top coating of epoxy or acrylic.

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United States Patent Number 4,421,620, issued to Kaylo et al. on December 20, 1983 (hereafter the '620 patent) discloses a process for preparing a corrosion-resistant metallic substrate by first anodically coating the substrate, and then, immediately, reversing the polarity of the coating cell and cathodically-coating the substrate with another layer of composition. The '620 patent, however, teaches that the substrate must remain electroconductive to a certain degree after being anodically-coated (see column 6, line 1). This requirement necessary prohibits the substrate from becoming totally insulated by anodic electrodeposition process and therefore limits the effectiveness of the anodic electrodeposition film.

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**Brief Summary of the Invention**

It is a general objective of the present invention to provide a method of coating a conductive substrate for the purposes of enhancing corrosion resistance and improving cosmetic appeal.

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It is a more specific objective of the present invention to provide a method of effectively electrodepositing an epoxy primer and an epoxy or acrylic top coat on small metallic parts in bulk quantities.

It is a related objective to provide a coated substrate possessing improved corrosion resistance characteristics and an enhanced physical appearance.

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Stated briefly, the inventive method utilized to produce the unique substrate comprises the sequential steps of anodically electrodepositing a first composition layer onto a metallic substrate, thermally curing said anodically coated substrate, and then cathodically electrodepositing a second composition layer onto said anodically coated substrate.

Detailed Description of the Invention

The coating method of the present invention constitutes a unique series of steps which result in providing a conductive substrate with corrosion protection properties and cosmetic appeal heretofore unattainable.

One important use of the coating method disclosed is in the art of coating small metallic fasteners in bulk quantities with epoxy films. Hereinafter, such art will be used for the purpose of explanation and illustration without intending to limit the applications and uses of the invention in any way. Moreover, while the invention will be described in connection with a preferred procedure, it will be understood that it is not intended to limit the invention to this procedure. On the contrary, the invention is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims.

The disclosed method is intended for use, however, only with substrates which are electrically conductive, which therefore are usually formed from some type of metallic substance. These pieces or parts to be coated may include a sacrificial metallic sub-coating such as zinc, cadmium, tin, etc. Standard pretreating methods including phosphate or chromate conversion coating, acid etching and grit blasting are recommended for initially cleaning the parts to be coated.

The inventive process begins by anodically electrodepositing a film, such as an epoxy onto the metallic substrates by placing the substrates in a coating unit or cell and imparting a positive electrical potential of approximately 50 to 250 volts onto the substrates. A negative electrical potential placed on cathodes within the coating unit, located at some predetermined distance away from the anodic substrates, creates a potential difference and causes a pH drop at the surface of the substrates. The pH drop in turn causes the epoxy present in the electrolyte to coat the surfaces of the substrates until a first, or "primer", coat of epoxy fully insulates the substrates. Preferably, the coated substrates are next rinsed to remove any excess coating. The anodic primer coat provides an ideal surface for the application of a second, or "top" coat of epoxy or acrylic, but is very susceptible to "touch points" or breaks in the coating caused by contact between multiple parts or with machinery. Moreover, a typical anodic primer coat affords only minimum corrosion protection.

Further in accordance with the inventive method, the anodically coated substrates are then removed from the coating cell and thermally cured. In the preferred procedure, thermal curing is accomplished by heating the parts to approximately 177°C (350°F) for a period of approximately 20 minutes. Thermal curing all but eliminates the possibility of "touch points" and ultimately improves cosmetic appearance of the coated substrates, as is more fully discussed below.

As a final step in the inventive method, the anodically coated substrates are re-immersed in an unspoiled coating cell and coated with a second, or "top" coating of epoxy by cathodic electrodeposition. This, of course, is accomplished in a manner similar to, but in reverse of an anodic electrodeposition process. That is, a negative electrical potential of between approximately 50 to 400 volts is placed on the substrates to be coated, said potential being sufficient to overcome the dielectric strength of the "primer" coat. A positive electrical potential is then placed on anodes located within the coating unit at some predetermined distance away from the now-cathodic substrates thereby causing the epoxy coating present in the unit to treat the surfaces of the substrates with a top coating of epoxy until the epoxy once again insulates the substrates and ends the top-coating process. The resultant coated substrates demonstrate corrosion resistance properties and cosmetic appeal heretofore unattainable by any known methods.

While it is not desired to be limited to any theory, the reason the above-described inventive method produces the superior results achieved appears to be related to the change in the dielectric strength of the "primer" coating of epoxy which occurs upon being thermally cured as described above. That is, the principle reason the anodically coated substrates can be top-coated seems to be because the cured anodic epoxy has a lower dielectric strength than the uncured anodic epoxy. This may be due to the presence of more non-conductive, space-filling water in the uncured epoxy than in the cured epoxy.

Whatever the reason, the result is that the substrates will accept a top-coating of epoxy by cathodic electrodeposition, which heretofore could not practically be accomplished.

It has also been found that the superior results achieved by the inventive method disclosed cannot be attained by first cathodically electrodepositing, curing and then anodically electrodepositing epoxy onto a substrates. The cured cathodic epoxy appears to have a much higher dielectric strength per unit thickness than the cured anodic epoxy.

After completing the inventive coating method, it is recommended that the parts be rinsed to remove any excess epoxy and then cured a second time at approximately 177°C (350°F) for approximately 20 minutes.

Examples of typical thicknesses for both the "primer" and "top" coatings are listed in Table I as follows:

TABLE I  
CM (In Inches)

5	Anodic Coatings:	0.000254 - 0.001016 (.0001-.0004)
	Cathodic coatings:	0.000254 - 0.001778 (.0001-.0007)
	Total:	0.000508 - 0.002794 (.0002-.0011)

Table II compares the results achieved by performing the inventive method disclosed with the results of various other methods:

Table II

15	<u>Coating Method</u>	<u>Corrosion Resistance*</u>	<u>Cosmetic Appearance</u>
	Anodic Only	<24 hrs.	Touch points and pinholes.
20	Cathodic Only	~48 hrs.	Touch points and pinholes.
25	Anodic/Anodic	<24 hrs.	Very few discernible marks in the film.
30	Inventive Method	~96 hrs.	Very few discernible marks in the film.

\* -- ASTM-B117 Neutral Salt Spray Test. Number shown indicates hours of exposure to red rust.

It should be noted that a cathodic/cathodic coating method results in a very thin "top" coating due to a propensity for the epoxy to evolve hydrogen at the surface of the substrates when the substrates are subjected to the required voltage. As a practical matter, this method is therefore not feasible.

#### Claims

1. A method of coating a conductive substrate comprising the sequential steps of:  
anodically electrodepositing a first composition layer onto said substrate;  
thermally curing said anodically coated substrate, and finally;  
cathodically electrodepositing a second composition layer onto said anodically coated substrate.
2. The method recited in claim 1, wherein the substrate to be coated receives a sacrificial conductive sub-coating prior to said anodic electrodeposition step.
3. The method recited in claim 1, wherein the substrate to be coated is pretreated before said anodic electrodeposition step, and rinsed after said anodic electrodeposition step and after said cathodic electrodeposition step.
4. The method recited in claim 1, wherein an electrical potential of between 50 to 250 volts is placed on the substrates during the anodic electrodeposition step.
5. The method recited in claim 1, wherein the thermal curing step is accomplished by heating the substrate

to approximately 177°C (350°F) and continuing said heating for approximately 20 minutes.

6. The method recited in claim 1, wherein an electrical potential of approximately 50 to 400 volts is placed on the substrate during the cathodic electrodeposition step.
- 5 7. The method recited in claim 1, wherein said first and second composition layers each comprise an epoxy or acrylic film.
8. The method recited in claim 1, wherein the thickness of said first composition layer is between approximately 0.000254 and 0.001016 cm. (.0001 and .0004 inches.)
- 10 9. The method recited in claim 1, wherein said second composition layer is between approximately 0.000254 and 0.001778 cm. (.0001 and .0007 inches.)
- 10 10. The method recited in claim 1, wherein the combined thickness of said first and second composition layers is approximately 0.000508 and 0.002794 cm. (.0002 to .0011 inches.)
- 15 11. The method recited in claim 1, wherein the conductive substrate comprises metal fasteners in bulk quantities.
- 20 12. The coated conductive substrate resulting from the performance of the method recited in claim 1.
13. A method of applying a coating to increase corrosion resistance and enhance the cosmetic appearance of a conductive material comprising the sequential steps of: anodically electrodepositing a primer coat, thermally curing said primer coat, and cathodically electrodepositing a top coat onto said anodically deposited primer coat.
- 25 14. A coated metallic fastener produced by performing the following sequence of method steps:  
anodically electrodepositing a first film onto said metallic fastener;  
thermally curing said anodically coated metallic fastener, and;  
then cathodically electrodepositing a second film onto said cured metallic fastener.
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#### Patentansprüche

- 35 1. Verfahren zur Beschichtung eines leitfähigen Substrates mit folgenden aufeinanderfolgenden Schritten:  
anodisches galvanisches Abscheiden einer ersten Kompositionsschicht auf dem Substrat,  
thermisches Härten des anodisch beschichteten Substrats und schließlich  
kathodisches galvanisches Abscheiden einer zweiten Kompositionsschicht auf dem anodisch beschichteten Substrat.
- 40 2. Verfahren nach Anspruch 1, worin das zu beschichtende Substrat vor dem Schritt des anodischen galvanischen Abscheidens eine leitfähige Opfer-Unterschicht erhält.
3. Verfahren nach Anspruch 1, worin das zu beschichtende Substrat vor dem Schritt des anodischen galvanischen Abscheidens vorbehandelt wird und nach dem Schritt des anodischen galvanischen Abscheidens und nach dem Schritt des kathodischen galvanischen Abscheidens gespült wird.
- 45 4. Verfahren nach Anspruch 1, worin während des Schrittes des anodischen galvanischen Abscheidens ein elektrisches Potential zwischen 50 und 250 Volt am Substrat angelegt wird.
- 50 5. Verfahren nach Anspruch 1, worin der Schritt des thermischen Härstens durch Erhitzen des Substrates auf etwa 177°C und Beibehaltung der Temperatur für ungefähr 20 Minuten ausgeführt wird.
6. Verfahren nach Anspruch 1, worin während des Schrittes des kathodischen galvanischen Abscheidens ein elektrisches Potential von etwa 50 bis 400 Volt am Substrat angelegt wird.
- 55 7. Verfahren nach Anspruch 1, worin die erste und zweite Kompositionsschicht jeweils einen Epoxy- oder Acrylfilm aufweist.

8. Verfahren nach Anspruch 1, worin die Dicke der ersten Kompositionsschicht zwischen etwa 0,000254 und 0,001016 cm beträgt.
9. Verfahren nach Anspruch 1, worin die Dicke der zweiten Kompositionsschicht etwa zwischen 0,000254 und 0,001778 cm beträgt.
10. Verfahren nach Anspruch 1, worin die kombinierte Dicke der ersten und zweiten Kompositionsschichten etwa zwischen 0,000508 und 0,002794 cm beträgt.
11. Verfahren nach Anspruch 1, worin das leitfähige Substrat metallische Befestigungselemente in Massengutmengen aufweist.
12. Beschichtetes leitfähiges Substrat, das gemäß dem Verfahren nach Anspruch 1 hergestellt ist.
13. Verfahren zum Aufbringen einer Beschichtung zur Erhöhung der Korrosionsbeständigkeit und Verbesserung der kosmetischen Erscheinung eines leitfähigen Materials mit den aufeinanderfolgenden Schritten: anodisches galvanisches Abscheiden einer Primärschicht, thermisches Härten der Primärschicht und kathodisches galvanisches Abscheiden einer Oberschicht auf die anodische Primärschicht.
14. Beschichteter metallischer Befestiger, hergestellt durch Ausführung der folgenden aufeinanderfolgenden Verfahrensschritte:
  - anodisches galvanisches Abscheiden eines ersten Films auf dem metallischen Befestiger,
  - thermisches Härten des anodisch beschichteten metallischen Befestigers und
  - kathodisches galvanisches Abscheiden eines zweiten Films auf dem gehärteten metallischen Befestiger.

#### Revendications

1. Procédé de revêtement d'un substrat conducteur, comprenant les étapes successives :
  - d'électrodéposition anodique d'une première couche de composition sur ledit substrat ;
  - de durcissement thermique dudit substrat portant un revêtement anodique et, finalement ;
  - d'électrodéposition cathodique d'une seconde couche de composition sur ledit substrat portant un revêtement anodique.
2. Procédé suivant la revendication 1, dans lequel le substrat à revêtir reçoit un sous-revêtement conducteur sacrificiel avant l'étape d'électrodéposition anodique.
3. Procédé suivant la revendication 1, dans lequel le substrat à revêtir est prétraité avant l'étape d'électrodéposition anodique, et rincé après ladite étape d'électrodéposition anodique et après l'étape d'électrodéposition cathodique.
4. Procédé suivant la revendication 1, dans lequel un potentiel électrique compris dans l'intervalle de 50 à 250 volts est appliqué aux substrats au cours de l'étape d'électrodéposition anodique.
5. Procédé suivant la revendication 1, dans lequel l'étape de durcissement thermique est effectuée par chauffage du substrat à approximativement 177°C (350°F) et ledit chauffage est continué pendant approximativement 20 minutes.
6. Procédé suivant la revendication 1, dans lequel un potentiel électrique d'approximativement 50 à 400 volts est appliqué au substrat au cours de l'étape d'électrodéposition cathodique.
7. Procédé suivant la revendication 1, dans lequel les première et seconde couches de composition comprennent chacune un film époxy ou acrylique.
8. Procédé suivant la revendication 1, dans lequel l'épaisseur de la première couche de composition est comprise dans l'intervalle d'approximativement 0,000254 à 0,001016 cm (0,0001 à 0,0004 inch).
9. Procédé suivant la revendication 1, dans lequel l'épaisseur de la seconde couche de composition est comprise dans l'intervalle d'approximativement 0,000254 à 0,001778 cm (0,0001 à 0,0007 inch).

10. Procédé suivant la revendication 1, dans lequel l'épaisseur totale des première et seconde couches de composition est comprise dans l'intervalle d'approximativement 0,000508 à 0,002794 cm (0,0002 à 0,0011 inch).
- 5 11. Procédé suivant la revendication 1, dans lequel le substrat conducteur comprend des attaches métalliques en grandes quantités.
12. Substrat conducteur revêtu par mise en oeuvre du procédé suivant la revendication 1.
- 10 13. Procédé d'application d'un revêtement pour accroître la résistance à la corrosion et améliorer l'aspect esthétique d'une matière conductrice, comprenant les étapes successives :  
d'électrodéposition anodique d'une couche de fond, de durcissement thermique de ladite couche de fond et d'électrodéposition cathodique d'une couche de finition sur ladite couche de fond formée par déposition anodique.
- 15 14. Attache métallique revêtue par mise en oeuvre de la série suivante d'étapes opératoires :  
électrodéposition anodique d'un premier film sur ladite attache métallique ;  
durcissement thermique de ladite attache métallique ayant été soumise à un revêtement anodique;  
puis  
20 électrodéposition cathodique d'un second film sur ladite attache métallique durcie.
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